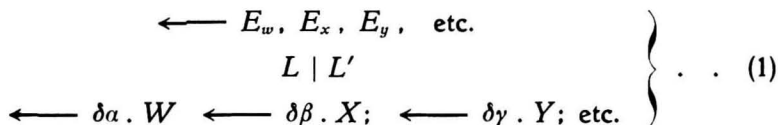**Chemistry**. — *Equilibria in osmotic systems, in which forces act. II. Osmotic systems, in which an active membrane, permeable for more substances.* By F. A. H. SCHREINEMAKERS.

In the preceding communication, which we shall call: "Comm. Act. Syst. I" in future, we have discussed systems, in which an active membrane, permeable for one substance only. We now take the general case viz. an active membrane permeable for more substances; for the sake of concentration we shall assume that this membrane performs a work E_w, E_x, E_y, etc. on every mol. W, mol. X, mol. Y etc. diffusing towards the left. If we now imagine that δa mol. W, $\delta\beta$ mol. X, $\delta\gamma$ mol. Y etc. diffuse towards the left, then we shall represent this system by:

$$\left. \begin{array}{c} \longleftarrow E_w,\ E_x,\ E_y,\ \text{ etc.} \\ L \mid L' \\ \longleftarrow \delta a\,.\,W \quad \longleftarrow \delta\beta\,.\,X; \quad \longleftarrow \delta\gamma\,.\,Y; \text{ etc.} \end{array} \right\} \quad . \quad . \quad (1)$$

If we now keep the volumina V and V' of the two liquids constant, then with this diffusion of δa mol. W, $\delta\beta$ mol. X etc. the free energy on the left side will increase with:

$$\left(\frac{\partial\psi}{\partial a}\right)_v \delta a + \left(\frac{\partial\psi}{\partial\beta}\right)_v \delta\beta + \left(\frac{\partial\psi}{\partial\gamma}\right)_v \delta\gamma + \ldots \quad . \quad . \quad . \quad . \quad (2)$$

On the right side of the membrane the free energy then will decrease with:

$$\left(\frac{\partial\psi'}{\partial a}\right)_{v'} \delta a + \left(\frac{\partial\psi'}{\partial\beta}\right)_{v'} \delta\beta + \left(\frac{\partial\psi'}{\partial\gamma}\right)_{v'} \delta\gamma + \ldots \quad . \quad . \quad . \quad (3)$$

With this diffusion the membrane performs a work $E_w\,\delta a + E_x\,\delta\beta + \ldots$ on the system; consequently we may say also that the system now performs an external work:

$$- E_w\,\delta a - E_x\,\delta\beta - E_y\,\delta\gamma \ldots \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As, according to GIBBS the free energy, augmented by the external work performed by the system, can only decrease or remain constant,

$$\left. \begin{array}{c} \left[\left(\dfrac{\partial\psi}{\partial a}\right)_v - \left(\dfrac{\partial\psi'}{\partial a}\right)_{v'} - E_w\right]\delta a + \left[\left(\dfrac{\partial\psi}{\partial\beta}\right)_v - \left(\dfrac{\partial\psi'}{\partial\beta}\right)_{v'} - E_x\right]\delta\beta + \\[4mm] + \left[\left(\dfrac{\partial\psi}{\partial\gamma}\right)_v - \left(\dfrac{\partial\psi'}{\partial\gamma}\right)_{v'} - E_y\right]\delta\gamma + \ldots \leqq 0 \end{array} \right\} \quad (5)$$

must consequently be satisfied.

If we now represent the internal O.W.A. by ξ_w and ξ'_w, the int. O.X.A. by ξ_x and ξ'_x, etc. then (5) passes into:

$$[\xi_w - \xi'_w + E_w] \, \delta a + [\xi_x - \xi'_x + E_x] \, \delta \beta + [\xi_y - \xi'_y + E_y] \delta \gamma + \ldots \gtreqless 0 \quad (6)$$

Instead of the volumina V and V' we may also keep the pressures P and P' on both sides of the membrane constant; (6) may then be deduced in a similar way as was indicated in Comm. Act. Syst. I for a membrane, permeable for one substance only.

Above we have assumed that the forces, working in the membrane, try to drive all substances towards the left; we may also imagine, however, that the membrane tries to drive one or more of these substances towards the right; we then have to substitute the corresponding $+E$ in (6) by $-E$. Instead of (6) we shall therefore write more generally:

$$[\xi_w - \xi'_w \pm E_w] \, \delta a + [\xi_x - \xi'_x \pm E_x] \, \delta \beta + [\xi_y - \xi'_y \pm E_y] \delta \gamma + \ldots \gtreqless 0 \quad (7)$$

Here we must give to E the positive or negative sign, according to the membrane trying to drive the corresponding substance towards the left or towards the right.

For the sake of brevity we now represent (7) by:

$$K_w \, \delta a + K_x \, \delta \beta + K_y \, \delta \gamma + \ldots \gtreqless 0. \quad\quad (8)$$

When the membrane tries to drive one of the substances S towards the left then we have, omitting the index s:

$$K = \xi - \xi' + E = \xi - (\xi' - E) \quad\quad\quad (9)$$

in which ξ and $\xi' - E$ now are the active O.S.A.; the substance S namely has a potential energy E on the right side of the membrane (comp. Comm. Act. Syst. I).

When the membrane tries to drive this substance S towards the right, we have instead of (9):

$$K = \xi - \xi' - E = (\xi - E) - \xi'. \quad\quad\quad (10)$$

As the substance S now has a potential energy on the left side of the membrane, the active O.S.A.'s now are $\xi - E$ and ξ'.

In the special case that no force acts on the substance S, we have:

$$K = \xi - \xi' \quad\quad\quad\quad\quad\quad (11)$$

so that the active O.S.A.'s now are ξ and ξ' and consequently both equal to the internal O.S.A.

From this it appears that in each of the imaginable cases (9), (10) and (11) K represents the difference between the active O.S.A.'s on the left and on the right side of the membrane. From this follows:

A) every coefficient K_w, K_x, K_y etc. of (8) represents the difference between the corresponding active O.W.A.'s on the left and on the right side of the membrane.

In the special case that system (1) is in equilibrium, the first part of (8) must be zero. When W, X, Y etc. now are substances, which cannot transmute, so that no relation exists between δa, $\delta \beta$ etc., then the equations:

$$K_w = 0; \quad K_x = 0; \quad K_y = 0; \text{ etc. } . \quad . \quad . \quad . \quad . \quad (12)$$

must be satisfied; their number is equal to the number of the diffusing substances. From this follows:

B) two liquids (gases etc.) between which an active or inactive membrane permeable for the substances W, X, Y etc., are in equilibrium with one another when they have the same active O.W.A., the same active O.X.A. etc.

In order to apply these considerations to a simple example, we take the osmotic system:

$$L . n . P . | M (n) | L' . n . P' . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

in which two liquids L and L' containing the same n substances; we represent the two pressures by P and P'; we imagine the membrane permeable for these n substances.

In order to simplify the discussion, we now shall take: $n = 3$; then we may represent the composition of these liquids by:

$$x \, mol \, X + y \, mol \, Y + (1 - x - y) \, mol \, W \quad . \quad . \quad . \quad (14)$$

$$x' \, mol \, X + y' \, mol \, Y + (1 - x' - y') \, mol \, W. \quad . \quad . \quad (15)$$

We now distinguish two cases.

When the membrane is inactive, it follows from (12) that the two liquids are in osmotic equilibrium with one another when:

$$\xi_w = \xi'_w; \quad \xi_x = \xi'_x; \quad \xi_y = \xi'_y . \quad . \quad . \quad . \quad . \quad (16)$$

If we now represent the therm. dyn. pot. of these liquids by Z and Z', then (16) passes into:

$$\left[Z - x \frac{\partial Z}{\partial x} - y \frac{\partial Z}{\partial y} \right]_P = \left[Z' - x' \frac{\partial Z'}{\partial x'} - y' \frac{\partial Z'}{\partial y'} \right]_{P'} \quad . \quad . \quad (17)$$

$$\left[Z + (1-x) \frac{\partial Z}{\partial x} - y \frac{\partial Z}{\partial y} \right]_P = \left[Z' + (1-x') \frac{\partial Z'}{\partial x'} - y' \frac{\partial Z'}{\partial y'} \right]_{P'} \quad . \quad (18)$$

$$\left[Z - x \frac{\partial Z}{\partial x} + (1-y) \frac{\partial Z}{\partial y} \right]_P = \left[Z' - x' \frac{\partial Z'}{\partial x'} + (1-y') \frac{\partial Z'}{\partial y'} \right]_{P'} \quad . \quad (19)$$

Now it is clear that these equations can be satisfied by:

$$x = x'; \; y = y' \text{ and } P = P' \quad \ldots \ldots \quad (20)$$

This means that the two liquids have the same composition and pressure. If we now assume, as we have always done until now, that no dimixtion into two or more liquids can occur, then we see that the 3 equations cannot be satisfied otherwise than by (20). As it appears from the deduction that this obtains also for every other value of n, it follows:

C_1) when an inactive membrane is permeable for all substances, then the two liquids will have the same composition and pressure at the end of the osmosis.

When the membrane is active, then:

$$\xi_w = \xi'_w \pm E_w; \; \xi_x = \xi'_x \pm E_x; \; \xi_y = \xi'_y \pm E_y \quad \ldots \quad (21)$$

must be satisfied, when the two liquids are in osmotic equilibrium with one another.

We now have to add the terms $\pm E_w$, $\pm E_x$ and $\pm E_y$ respectively to the second part of the equations (17)—(19).

Now it is clear that, even when one or two of the potential energies should be zero, these equations can never be satisfied by (20). From this follows:

C_2) when an active membrane is permeable for all substances, then the two liquids have a different composition and pressure at the end of the osmosis.

Only in very special cases, namely when a definite relation exists between the potential energies etc., either the composition or the pressure may accidentally be the same.

The number of freedoms.

In the osmotic system:

$$L.\, n.\, P. \mid M\,(d) \mid Syst.\, a.\, P_a \quad \ldots \ldots \quad (22)$$

we have on one side of the membrane a liquid L, containing n substances, under the pressure P; on the other side a given system a of one, two or more phases, which has a definite composition and pressure P_a. In the special case that this system a consists of one single phase only, e.g. of a liquid or a gas, we may represent it by:

$$L.\, n.\, P \mid M\,(d) \mid Liq.\, a.\, P_a \quad \ldots \ldots \quad (23)$$

$$L.\, n.\, P \mid M\,(d) \mid Gas\, a.\, P_a \quad \ldots \ldots \quad (24)$$

We now may put the question: which conditions have to be satisfied by the composition and the pressure of liquid L, for to be in osmotic equilibrium with the given system a.

If we now assume that d substances may diffuse, then these substances

must of course also be present in the given system a; when this system contains besides also non-diffusing substances, these may or may not be the same as those of liquid L.

We may represent the composition of liquid L, containing n substances, by $n{-}1$ variables; as we shall look upon pressure P also as a variable, liquid L has, therefore, been completely determined by n variables.

When d substances diffuse, these n variables must satisfy the d equations (12); so liquid L has

$$n{-}d \; freedoms \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

As the number of non-diffusing substances of liquid L is also $n{-}d$, we may say therefore :

D) the number of freedoms of a liquid, which is in osmotic equilibrium with a given system, is equal to the number of the non-diffusing substances of this liquid. In this case it does not matter whether the membrane is active or inactive.

In order to apply this rule, we shall distinguish different cases.

When all substances of the liquid L diffuse : $n{-}d = 0$; consequently the liquid has no freedom. From this follows :

E_1) when a liquid, of which all substances can diffuse, is in osmotic equilibrium with a given system, its composition and pressure must be completely determined.

When liquid L contains one non-diffusing substance, then $n{-}d = 1$; consequently it has one freedom. From this follows :

E_2) when a liquid, containing one non-diffusing substance, is in osmotic equilibrium with a given system, it can exist under quite a series of pressures; under each pressure this liquid will then have a definite composition, changing with the pressure.

When liquid L contains two or more non-diffusing substances, $n{-}d \gtreqless 2$; consequently it has two or more freedoms; from this follows :

E_3) when a liquid, containing two or more non-diffusing substances, is in osmotic equilibrium with a given system, it can exist under quite a series of pressures; then the liquid may have an infinite number of compositions under each of these pressures.

The above obtains as well for active as for inactive membranes; it is clear, however, that the pressures and compositions, mentioned in E_1, E_2 and E_3 will be quite different, when the membrane is active than when it is inactive (comp. e.g. C_1 and C_2); we shall refer to this later on, when discussing the osmosis.

In the osmotic system

$$l. \; Syst. \; n. \; r. \; P \mid M \, (d) \mid Syst. \; a. \; P_a \quad . \quad . \quad . \quad . \quad . \quad (26)$$

we have once more a given system a on the right side of the membrane; on the left side is a system of n substances in r phases under the pressure P; we shall call this the l. system. We may imagine that (26) has e.g.

sprung from (22) when we add one or more phases (e.g. a vapour or solid substances) to the liquid L in (22).

When the phases of this l. system are in equilibrium with one another, the potential of the substance X must have the same value in all phases containing this substance X; the same obtains also for the other substances. It now follows from the meaning of ξ_x, ξ_y etc. that all phases have the same ξ_x, the same ξ_y etc. When e.g. the substance X occurs in three phases, which we call 1, 2 and 3, then is, therefore:

$$(\xi_x)_1 = (\xi_x)_2 = (\xi_x)_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

If we now take into consideration the number of variables of the l. system and the number of equations, then we find, what is in accordance with GIBBS' well-known rule, that this l. system has

$$n - r + 1 \ \textit{freedoms.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Here we have assumed that the temperature was constant. When in the osmotic system (26) d substances diffuse, so that there are d equations (12) besides, we might conclude:

F) the l. system of the osmotic system (26) has:

$$n - r + 1 - d \ \textit{freedoms} . \quad . \quad . \quad . \quad . \quad (29)$$

This rule obtains only, however, when each of the d equations (12) reduces the number of freedoms of the l. system with one; as this is not always the case, however, as we shall see further on, we must be very careful in applying this rule and first consider every special case more closely. We shall illustrate this with some examples.

When e.g. the l. system contains the solid substance X, then $\xi_x = - Z$ in which Z_x is the thermodyn. pot. of the solid X; as Z_x only depends upon the pressure P, we have, therefore:

$$\xi_x = \varphi_x(P) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

in which φ_x is a definite function, dependent on the nature of substance X.

We shall begin by assuming that pressure P of the l. system is still variable.

When X is one of the diffusing substances, then, as follows from (12), we have:

$$\xi_x = \xi'_x \pm E_x . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

in which E_x may or may not be zero. It now follows from (30) and (31) that

$$\varphi_x(P) = \xi'_x \pm E_x \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

must be satisfied now.

As system a and consequently also the second part of (32) is known, the pressure P has consequently also been determined. From this follows:

G) when one of the diffusing substances occurs as a solid phase in the l-system, then no matter how large the number of freedoms is, we cannot choose pressure *P* arbitrarily [1]), for this pressure is completely determined by the active O. X. A. of the given system. *a.*

This obtains also when instead of the solid phase there is a gaseous one, containing one single substance only, e.g. *W*-vapour.

When the l- system contains two solid phases e.g. *X* and *Y*, then, when both substances diffuse, (32) must be satisfied and :

$$\varphi_y (P) = \xi'_y \pm E_y \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

As, however, *P* has already been determined by (32), (33) can be satisfied only when the second part has a definite value. So equation (33) does not limit the number of freedoms of the l- system, but it makes a condition which must be satisfied by the active O. Y. A. of the given system *a*. From this it appears that we may say in general :

H) when in the l. system *q* of the diffusing substances are present as solid phases, they reduce the number of freedoms of the l. system with "One" only ; they make *q*—1 conditions, however, which must be satisfied by system *a.*

The reader may apply corresponding considerations to other cases e.g

when pressure *P* of the l. system has been given or has been determined already by the nature of the l. system itself

or when the number of freedoms, arising from (29) is negative ;

and also to the general osmotic system

$$l.\ Syst.\ n.\ r.\ P\ |\ M\,(d)\ |\ r.\ Syst.\ n'.\ r'.\ P'.\quad . \quad . \quad . \quad . \quad (34)$$

which we may imagine as having arisen from (26), by substituting the given system *a* in it by an arbitrary system of *x'* substances in *r'* phases under a pressure *P'*.

It is now easy to find that we might conclude that this osmotic system has :

$$(n + n') - (r + r') + 2 - d\ freedoms\ . \quad . \quad . \quad . \quad (35)$$

Corresponding and other observations obtain here, however, as were mentioned above in connection with (29) so that we must examine every given case more closely ; then it will also be possible to indicate how the real freedoms are divided over the *l.*- and the *r.* system.

(To be continued.)

Leiden Lab. of Inorg. Chemistry.

---

[1]) Corresponding cases for *P* and *T* may also occur in systems in which no substances diffuse. Compare F. A. H. SCHREINEMAKERS, deze Verslagen 25, 535, 627 (1916); 25, 754, 860, 939, 1102 (1917); these Proceedings 19, 514, 713, 816, 867, 927, 999 (1917).